# (19) World Intellectual Property Organization International Bureau



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(43) International Publication Date 25 September 2003 (25.09.2003)

**PCT** 

# (10) International Publication Number WO 03/078531 A1

(51) International Patent Classification<sup>7</sup>: 5/02, 133/06, 109/00, 5/32

C09D 5/24,

- (21) International Application Number: PCT/US02/07039
- (22) International Filing Date: 8 March 2002 (08.03.2002)
- (25) Filing Language:

English

(26) Publication Language:

English

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- (81) Designated States (national): AB, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DH, DK, DM, DZ, BC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, FH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

#### Published:

with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

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(54) Title: ELECTRICALLY CONDUCTIVE AND ELECTROMAGNETIC RADIATION ABSORPTIVE COATING COMPOSITIONS AND THE LIKE

(57) Abstract: A coating composition having outstanding electrically conductive and/or electromagnetic radiation absorptive properties is disclosed with a water soluble emulsion polymer binder. The binder is a blend of a first emulsion containing a conjugated diene as monomer or comonomer, and a second emulsion containing an acrylic polymer. An effective amount of electrically conductive particles is dispersed in the binder. The particles include a combination of graphite particles, and metal containing particles. A solvent effective amount of water is also present.

# ELECTRICALLY CONDUCTIVE AND ELECTROMAGNETIC RADIATION ABSORPTIVE COATING COMPOSITIONS AND THE LIKE

#### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

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The present invention is directed to electrically conductive and electromagnetic radiation absorptive coating compositions and the like.

#### 2. Brief Description of the Prior Art

A variety of coating compositions are known which have electrically conductive or electromagnetic radiation absorptive properties or the like. The solvent for many of the coating compositions has been primarily a volatile organic compound (VOC). A VOC-based binder system has several drawbacks. It may be toxic, flammable, and possibly explosive. The VOC raw material is costly to purchase and the waste is expensive to discard. Generally, VOC solvent emitted from coating operations is an environmental air pollutant. Expensive equipment and procedures are required to capture and contain VOC solvent emissions in order to reduce air pollution and enable proper waste disposal.

Coating compositions are also known which use electrically conductive or electromagnetic radiation absorptive

microspheres. However, these coating compositions have been limited by the binder systems employed.

Finally, coating compositions are known which use a plurality of electrically conductive particles. However, these coating compositions have also been limited by the binder systems employed.

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Accordingly, it is an object of the present invention to provide an aqueous based coating composition having electrically conductive or electromagnetic radiation absorptive properties or the like.

It is a further object of the present invention to provide a coating composition which is electrically conductive or electromagnetic absorptive or the like having an improved binder system.

It is another object of the present invention to provide an aqueous based coating composition having electrically conductive and electromagnetic radiation absorptive properties particularly useful for coating plastic surfaces, flexible plastic objects and other flexible materials as well as metal surfaces and the like.

These and other objects of the invention will become more apparent upon reading the following description of the invention.

#### SUMMARY OF THE INVENTION

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The present invention is directed to an electrically conductive and/or electromagnetic radiation absorptive coating composition or the like having a water soluble emulsion polymer binder. The binder is a blend of a first emulsion containing a conjugated diene monomer or comonomer, and a second emulsion containing an acrylic polymer. The first emulsion preferably includes an ethylenically unsaturated comonomer which is typically an unsaturated nitrile such as acrylonitrile, a monovinyl aromatic hydrocarbon such as styrene, or vinylpyridine. The first emulsion is preferably a substantially saturated carboxylated or non-carboxylated butadiene-acrylonitrile latex. The carboxylated butadiene-acrylonitrile latex preferably contains unreacted salts. The second emulsion is an acrylic latex.

The coating composition also contains an effective amount of electrically conductive particles dispersed in the binder. The particles include a combination of graphite particles and metal containing particles. The graphite particles are preferably natural flake graphite. The metal containing particles are preferably silver or nickel containing particles. The silver or nickel containing particles are more preferably silver or nickel containing particles are more preferably silver or nickel coated ceramic microspheres which may have electromagnetic radiation absorptive properties.

The coating composition also contains water. The water is present in a solvent effective amount.

The present invention further relates to a coated substrate. The substrate is typically paper, cloth, plastics such as polycarbonate, acrylic, nylon, polyester, rubber, steel, composite materials or fiberglass. The substrate may be a plastic component of an electronic device. The substrate may also be a pipe, a rubber mat, or the like. In the case where the metal containing particles are electromagnetic radiation absorptive microspheres, the substrate is typically a vehicle such as an aircraft, tank or ship.

### DESCRIPTION OF THE PREFERRED EMBODIMENTS

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Although several preferred compositions of the present invention are disclosed, it is to be understood that the exact compositions are given by way of illustration only. It is not intended that the invention be limited in its scope to the exact compositions set forth in the following description. Also, in describing preferred compositions, specific terminology will be resorted to for the sake of clarity. It is to be understood that each specific term includes all technical equivalents.

The first emulsion of the coating composition includes polymers composed of 5 to 100% by weight of a conjugated diene monomer unit and 95 to 0% by weight of an ethylenically unsaturated monomer unit. Specific examples of the conjugated

diene monomer are 1,3-butadiene, 2,3-dimethylbutadiene, isoprene and 1,3-pentadiene. Specific examples of the ethylenically unsaturated monomer include unsaturated nitriles such as acrylonitrile and methacrylonitrile, monovinyl hydrocarbons such as styrene and alkylstyrenes, divinyl aromatic hydrocarbons such as divinylbenzene, dialkenyl aromatics such as diisopropenylbenzene, unsaturated carboxylic acids and the esters thereof such as acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid, methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate and methyl methacrylate; vinylpyridine; and vinyl esters such as vinyl acetate. polymer may be one hydrogenated by the method described in U.S. Patent No. 4,452,950, the disclosure of which is expressly incorporated herein by reference.

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Specific examples of polymers include nitrile butadiene, styrene butadiene, butadiene reacted with vinyl pyridine, polybutadiene, carboxylated nitrile butadiene and carboxylated styrene butadiene. A preferred polymer is a highly saturated butadiene/acrylonitrile copolymer latex available from the Goodyear Tire and Rubber Company, Akron, Ohio ("Goodyear") as Chemisat LCH-7302X latex. Another preferred polymer is a highly saturated carboxylated butadiene/acrylonitrile latex available from Goodyear as Chemisat LCH-7505X latex. The carboxylated commercial product contains unreacted salts which

are believed to be particularly beneficial to the present invention.

The second emulsion is an acrylic latex. Suitable acrylic emulsions are available from Rohm and Haas Company, Philadelphia, Pennsylvania as Rhoplex® WL-96 waterborne acrylic polymer and Maincote® HG-54D waterborne acrylic resin.

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The blending of the second or acrylic emulsion with the first emulsion results in several desirable properties and improvements in the characteristics of the first emulsion. The acrylic emulsion enhances the chemical resistance of the first emulsion, improves its hardness while retaining its flexibility, enhances its adhesion properties to create a stronger bond with a substrate, and makes the resulting blend smoother. The use of the acrylic emulsion may also improve the exterior durability of the first emulsion as well as its abrasion resistance.

The graphite particles are preferably natural flake graphite. Suitable natural flake graphite particles are available from the Ashbury Graphite Mills, Inc., Ashbury, New Jersey, having a particle size of about 97% or greater passing 325 mesh U.S. Standard Sieve, i.e. less than 44 microns. These particles contain about 95% or greater carbon. The particles are available under the grade numbers 146, Micron 750 and Micron 790.

The metal containing particles are preferably silver or nickel containing particles; however, other metals may also be employed such as gold, platinum and palladium. The metal

containing particles are more preferably metal coated ceramic microspheres.

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As disclosed in U.S. Patent Nos. 4,624,798 and 4,624,865, the disclosures of which are expressly incorporated herein by reference, electrically nonconductive magnetic microballoons or microspheres may be coated with an extremely thin layer of metal to produce a material which can be incorporated into electrically nonconductive materials to give composites with superior electrical conductivity. These composites have a very low density, often lower than the electrically nonconductive plastic. Additionally, the desirable mechanical properties of the composite are only slightly affected by the inclusion of metal coated magnetic microballoons. As known to those skilled in the art, the terms "microspheres" and "microballoons" are interchangeable and connote the same product and technology.

As further disclosed in the '798 and '865 patents, certain grades of commercially available ceramic microballoons have inherent magnetic properties. The magnetic properties are attributable to the presence in the ceramic composition of magnetic components such as iron, nickel, iron oxide, ferrite or mixtures of these materials. This magnetic property enhances the tendency of the metal coated microballoons to form networks, and gives composites with exceptional electrical conductivity.

'798 and '865 patents disclose the use of The which microballoons are ceramic available commercially lightweight, strong microspheres formed of a ceramic composition composed primarily of aluminum silicates, magnesium silicates, sodium silicates, or mixtures of these materials. The microspheres are hollow, have a porous ceramic shell, and are considerably stronger and more abrasion resistant than siliceous (glass) hollow microspheres. More particularly, these ceramic microspheres, which are referred to as "centospheres", are derived from the ash from industrial furnaces which burn powdered coal, and certain grades of them are magnetic as a consequence of the coal containing magnetic impurities such as iron, ferrite, nickel, ferric oxide and magnetite. Since they are a byproduct of coal-fired furnaces, they are considerably less expensive than commercially manufactured microballoons.

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According to the '798 and '865 patents, noble metals such as silver, gold, platinum, and palladium give the best results, having a negligible tendency to oxidize at the contact points. By providing a thin coating of the noble metal on the surface of an inexpensive and lightweight magnetic microballoon, it is said to be possible to achieve the desirable electrical properties of the metal. The microballoons are preferably coated with silver.

According to U.S. Patent No. 5,786,785, the disclosure of which is expressly incorporated herein by reference, metal

coated microspheres of the type described in U.S. Patent Nos. 4,624,798 and 4,624,865 can be used to form strong, very lightweight coatings and composites which absorb electromagnetic radiation. The microspheres have a diameter of from 1 to 350 microns, and the microballoons contain at least one radiation absorbing material selected from the group consisting of carbon, ferrites, magnetite, iron, nickel and cobalt and have a thin coating of metal on the microsphere surface. Preferably, the '785 patent states the microspheres comprise ceramic magnetic microspheres derived from the ash from coal fired furnaces, and these microspheres possess permanent magnetic properties.

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According to the '785 patent, the microspheres are coated with a thin coating of an electrically conductive metal on the microsphere surface, the metal coating being present in a percentage by weight of 0.01 to 22 percent. While any conductive metal may be used, silver, gold, platinum, palladium and their alloys are preferred. The microspheres are plated with the metal using the procedures described in U.S. Patent Nos. 4,624,798 and 4,624,865.

For best results, the '785 patent states the coating should be electrically isolated from an electrically conductive substrate by a coating of insulator material applied as a primer. The thickness of the primer and its electrical properties become less important as the thickness of the absorptive layer increases. The absorptive layer may be top coated to give a very

tough and smooth final surface with any conventional coating which is radar transparent.

Microspheres of the type described above are commercially available from Spectro Dynamic Systems, Hickory, North Carolina. These microspheres include silver coated cenospheres having particle sizes of 5 to 75 microns in diameter and typical silver thickness of 500 angstroms.

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The combination of graphite particles with metal containing particles avoids certain detrimental characteristics found in the prior art. In materials utilizing graphite as a conductive component, the amount of graphite required to produce adequate conductivity may result in an undesirable decrease in film-forming properties. Also, metal particles are very dense compared to the typical polymer used as a binder and tend to settle out and separate from the binder. By using a combination of graphite and metal containing particles, a sufficient amount of binder may be used to provide the desirable film-forming (e.q., adhesion, film integrity, flexibility, properties while obtaining improved conductivity. durability) In particular, when graphite particles are used in combination with metal coated microspheres, it is believed that the graphite particles fill in the gaps between the microspheres to provide improved electrical conductivity properties.

The polymer blend also includes water. The water is present in a solvent effective amount.

The coating composition will typically contain about 10-600 parts by weight of the first emulsion, preferably about 300-500 parts by weight. The coating composition will typically contain about 10-600 parts by weight of the second emulsion, preferably about 100-300 parts by weight. composition will typically contain about 1-280 parts by weight of the graphite particles, preferably about 20-200 parts by weight. The coating composition will typically contain about 1-280 parts by weight of the metal containing particles, preferably about 20-200 parts by weight. The coating composition will also typically contain, in addition to any water which is present in the binder system, about 50-150 parts by weight of water, preferably about 75-125 parts by weight. The coating composition may also include various additives such as tetrafluoroethylene fluorocarbon polymers, thickening agents, dispersants, coalescing solvents and anti-foaming agents, in amounts conventionally employed in these types of compositions.

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The binder system described herein which includes a blend of the first and second emulsions may be used as a primer or top coat for the coating composition of the present invention. Alternatively, conventional primers and top coats may be employed in combination with the coating composition of the present invention depending upon the desired use of the product. For example, an acrylic latex may be used as a top coat for the coating composition of the present invention.

The present invention provides an excellent coating for paper and other similar substrates. It offers excellent resistance to heat, solvent, gasoline, aging, ozone, ultraviolet light, oxygen and fluid while being aqueous based. It requires no hydrogen, solvents, expensive catalysts or special equipment. Its heat aging is superior to conventional nitrile butadiene rubber and can be formulated in dip systems or beater additions. It also has good low temperature flexibility and excellent flex fatigue resistance. This product has a low VOC content and is non-flammable. It has an excellent dry time of about 20 minutes tack free and can be force-dried.

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The coating composition of the present invention can also be coated on a variety of substrates, in addition to paper. The other substrates include cloth, plastics such as polycarbonate, acrylic, nylon, polyester, rubber, steel, composite structures and fibers such as aramid and glass.

The application of the coatings to substrates is simple and straightforward. The substrates can be brushed, sprayed, rolled or roll coated. In addition, the substrates can be coated by dip application. In dip applications, several dipping operations will be required to achieve the necessary film thickness (e.g., 2-10 mils). After each dip application, forced air drying should be used. In order to perform as a coating composition, the coating formulations according to the present invention have a viscosity ranging between 15 and 66 seconds with

a #2 Zahn cup, or about 10 to about 350 centipoise. Preferably, the viscosity of the coating composition of the present invention ranges between 20 and 40 seconds with a #2 Zahn cup, or about 32 to about 95 centipoise. Further, the coating composition of the present invention cures at temperatures consistent with ambient conditions and within a reasonable time frame so as to facilitate its application and use as a coating composition. More specifically, the composition of the present invention cures at temperatures between about 50°F and about 120°F, and preferably between about 60°F and about 100°F. The cure time ranges between about 10 minutes and about 6 hours, and preferably between about 30 minutes and about 1.5 hours.

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The % nonvolatile component of the coating composition of the present invention should range between about 35.0 and about 60.0 (by weight) and about 25.0 to about 45.0 (by volume), preferably ranging between about 40.0 to about 50.0 (by weight) and 30.0 to about 40.0 (by volume). Other specifications of the coating composition of the present invention are typically:

Wgt. per gal: 8.1 - 8.5

% Wgt. solids: 40.0 - 50.0

% vol. solids: 30.0 - 50.0

% Saturation: 94±2

Surface Tension d/cm 36

pH: 9.8 - 10.2

The composition of the present invention also can be used for the coating of paper by beater addition to strengthen and fortify the paper fiber to make it chemically resistant. This method can produce coatings to protect gaskets and paper from the effects of transmission fluids, gasolines, oil, and heat to temperatures of 350°F. A beater is a special machine used to open and disperse by mechanical action the fiber bundles in a dilute slurry of pulp. The dispersed fibers are then shortened and fibrillated by continuing the action of the beater before adding the coating material of the present invention. Once added to the beater or to a downstream mixing tank, the coating material is precipitated under controlled conditions by reaction with alum or cationic agents such as water soluble polyamides or polyamines. Dilute aqueous aluminum sulfate solutions are used to completely precipitate the coating material from the highly diluted slurry onto the fiber and fillers. Once the latex precipitation is complete, the stock or "furnish", as it may be called, is fed to a machine chest and into the paper machine. Once this process is completed, the paper fibers are further coated with the coating of the present invention.

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The coatings of the present invention have tremendous adhesion properties and performance to a variety of substrates. The coatings have unique conductive and shielding properties. For example, a paper circuit board coated with this water-based system can effectively conduct electricity and shield electronic

devices from stray electrical currents. The coatings can also be used as water-based decontaminable coatings for military applications. The coatings also have high military value in stealth technology for hiding ships, planes, etc.

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The chemistry of the present invention is based on a combination of acrylic waterborne resins in combination with water-based conjugated diene monomer or comonomer rubber resins which has created a unique combination of chemical resistance and adhesion properties. The incorporation of conductive particles has enhanced the electrical properties. Also, one of the resins has about 6% unreacted conductive salts that adds to its conductive properties.

Illustrative end uses include the following:

- 1) electrical conductive and shielded paper;
- 2) chemical warfare resistant coatings for paper, plastic, cloth, steel, fiberglass, etc.;
- 3) plastics components for computers, electronic devices shielded from stray radio waves and electrical impulses:
- 4) coated plastic pipe, rubber, and plastic to dissipate electrical charges built up during transferring of flammable liquids or in explosive environments;
  - 5) electrical and shielded rubber water-based coatings;

6) water-based shielded electrical coating systems with chemically decontaminable water-based systems for bacteriological warfare;

- 7) use of the above coating systems to provide stealth characteristics for military applications for tanks, planes, jeeps, ships, etc.;
- 8) use of the above coating systems on radar domes, antennae, computers, etc. for shielding and static electrical dissipation; and
- 9) application to rubber mats for grounding of electrical devices and computers.
  - 10) application to surfaces of a room, such as the walls, ceiling and/or floor, for eavesdropping prevention.

The following examples illustrate coating compositions in accordance with the present invention which have electrically conductive and electromagnetic radiation absorptive properties using graphite and silver coated ceramic microspheres.

### EXAMPLE 1

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| 0 | Composition<br>Component        | Weight in<br>parts per 100/Wt. |
|---|---------------------------------|--------------------------------|
|   | Acrylic Resin #1                | 37.5                           |
|   | XHNBR Latex #1                  | 5.5                            |
|   | Water                           | 12.5                           |
|   | Ethylene Glycol Monobutyl Ether | 5.0                            |
| 5 | Defoamer #1                     | 1.0                            |

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|--------------------|------|
| Surfactant         | 1.0  |
| Conductive Spheres | 35.0 |
| Graphite           | 2.5  |

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The Acrylic Resin #1 was placed in a suitable vessel for mixing and slow speed agitation was begun. The XHNBR Latex #1 was added at a slow rate and allowed to mix with the Acrylic Resin for 5 minutes. Water and glycol ether were premixed in a separate container and added slowly to the vessel containing the resins under agitation. The defoamer and surfactant were then added and allowed to mix for 15 minutes under mild agitation. Next, the conductive spheres were slowly added with continued mild agitation, while allowing the spheres to wet out completely. The graphite was then added slowly under mild agitation, and the entire mixture continued to mix for 20 minutes under mild agitation. The coating formulation of Example 1 is particularly useful for coating on plastic surfaces and exhibited the following properties:

Flexibility Pass 1/4" Mandrel Bend Test according to ASTM
D522

20 Conductivity 1.5 ohms per square

Impact resistance Pass 160 in/lb direct and 160 in/lb reverse impact test according to ASTM D2794

Viscosity 38 seconds using a #2 Zahn Cup according to ASTM D4212

#### 25 EXAMPLE 2

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|    | Composition<br><u>Component</u> |                     | Weight in parts per 100/Wt. |
|----|---------------------------------|---------------------|-----------------------------|
|    | Acrylic Resin                   | #1                  | 35.0                        |
|    | XHNBR Latex #1                  |                     | 8.0                         |
| 5  | Water                           |                     | 12.5                        |
|    | Ethylene Glyco                  | l Monobutyl Ether   | 5.0                         |
|    | Defoamer #1                     |                     | 1.0                         |
|    | Surfactant                      |                     | 1.0                         |
|    | Conductive Sph                  | eres                | 30.0                        |
| 10 | Graphite                        |                     | 7.5                         |
|    | The composition of I            | Example 2 was formu | lated in the same procedure |
|    | as described abov               | e in connection     | with Example 1. This        |
|    | composition is par              | ticularly useful :  | for flexible plastics and   |
|    | exhibited the follo             | wing properties:    |                             |
| 15 | Flexibility                     | Pass 1/4" Mandrel   | Bend Test according to ASTM |
|    |                                 | D522                |                             |
|    | Conductivity                    | 2.2 ohms per squa   | re                          |
|    | Impact resista                  | nce Pass 160 in     | /lb direct and 160 in/lb    |
|    |                                 | reverse impact te   | st according to ASTM D2794  |
| 20 | Viscosity                       | 40 seconds using    | a #2 Zahn Cup according to  |

## EXAMPLE 3

|    | Composition Component | Weight in<br>parts per 100/Wt. |
|----|-----------------------|--------------------------------|
| 25 | Acrylic Resin #1      | 31.0                           |

ASTM D4212

| WO 03/078531 |                                 | PCT/US02/07039 |  |
|--------------|---------------------------------|----------------|--|
|              | XHNBR Latex #1                  | 11.0           |  |
|              | Water                           | 12.5           |  |
|              | Ethylene Glycol Monobutyl Ether | 5.0            |  |
|              | Defoamer #1                     | 1.0            |  |
| 5            | Surfactant                      | 1.0            |  |
|              | Conductive Spheres              | 32.0           |  |
|              | Graphite                        | 5.5            |  |

The composition of Example 3 was formulated in the same procedure as described above in connection with Example 1. This composition is particularly useful for flexible materials such as paper and textiles and exhibited the following properties:

Flexibility Pass 1/8" Mandrel Bend Test according to ASTM
D522

Conductivity 1.7 ohms per square

Impact resistance Pass 160 in/lb direct and 160 in/lb
reverse impact test according to ASTM D2794
Viscosity 38 seconds using a #2 Zahn Cup according to
ASTM D4212

### EXAMPLE 4

| 30 | Composition Component             | Weight in parts per 100/Wt. |
|----|-----------------------------------|-----------------------------|
|    | Acrylic Resin #2                  | 38.0                        |
|    | XHNBR Latex #1                    | 7.5                         |
|    | Water                             | 9.0                         |
| :5 | Diethylene Glycol Monobutyl Ether | 5.0                         |

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|--------------------|----------------|
| Defoamer #2        | 1.0            |
| Surfactant         | 1.0            |
| Conductive Spheres | 30.0           |
| Graphite           | 7.5            |

The composition of Example 4 was formulated in the same procedure as described above in connection with Example 1 except that Acrylic Resin #2 and Defoamer #2 were substituted for Acrylic Resin #1 and Defoamer #1, respectively. This composition is particularly useful for metal surfaces and exhibited the following properties:

Flexibility Pass 1/4" Mandrel Bend Test according to ASTM D522

Conductivity 2.2 ohms per square

Impact resistance Pass 160 in/lb direct and 160 in/lb reverse impact text according to ASTM D2794

Viscosity 38 seconds using a #2 Zahn Cup according to

ASTM D4212

#### EXAMPLE 5

| 20 | Composition<br>Component          | Weight in parts per 100/Wt. |
|----|-----------------------------------|-----------------------------|
|    | Acrylic Resin #2                  | 35.0                        |
|    | XHNBR Latex #1                    | 10.5                        |
|    | Water                             | 10.0                        |
|    | Diethylene Glycol Monobutyl Ether | 5.0                         |
| 25 | Defoamer #2                       | 1.0                         |

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|---|-----------------------|
| Surfactant                                  | 1.0                   |
| Conductive Spheres                          | 35.0                  |
| Graphite                                    | 2.5                   |
| The composition of Example 5 was formulated | in the same procedure |
| as described above in connection with       | Example 4. This       |
| composition is particularly useful for i    | flexible plastic and  |

composite structures and exhibited the following properties:

Flexibility Pass 1/8" Mandrel Bend Test according to ASTM

10 Conductivity 1.5 ohms per square

D522

Impact resistance Pass 160 in/lb direct and 160 in/lb reverse impact test according to ASTM D2794

Viscosity 34 seconds using a #2 Zahn Cup according to ASTM D4212

### 15 EXAMPLE 6

|    | Composition<br>Component        | Weight in parts per 100/Wt. |
|----|---------------------------------|-----------------------------|
|    | Acrylic Resin #1                | 35.0                        |
|    | XHNBR Latex #2                  | 8.0                         |
| 20 | Water                           | 12.5                        |
|    | Ethylene Glycol Monobutyl Ether | 5.0                         |
|    | Defoamer #1                     | 1.0                         |
|    | Surfactant                      | 1.0                         |
|    | Conductive Spheres              | 30.0                        |
| 25 | Graphite                        | 7.5                         |

The composition of Example 6 was formulated in the same procedures as described above in connection with Example 1, except XHNBR Latex #2 was substituted for XHNBR Latex #1. This composition is particularly useful for plastics and composites and exhibited the following properties:

Flexibility Pass 1/4" Mandrel Bend Test according to ASTM
D522

Conductivity 2.2 ohms per square

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Impact resistance Pass 160 in/lb direct and 160 in/lb reverse impact test according to ASTM D2794

Viscosity 36 seconds using a #2 Zahn Cup according to
ASTM D4212

The following is a list of sources for the various compositions used in the above six examples.

- 1) Acrylic Resin #1 was "Rhoplex WL-96," which is a waterborne acrylic polymer available from Rohm & Haas Co., Philadelphia, Pennsylvania.
  - 2) Acrylic Resin #2 was "Maincote HG-54D," which is a waterborne acrylic resin available from Rohm & Haas Co., Philadelphia, Pennsylvania.
  - 3) XHNBR Latex #1 was "Chemisat LCH-7302X," which is a highly saturated butadiene/acrylonitrile copolymer latex available from the Goodyear Tire & Rubber Co., Akron, Ohio.

4) XHNBR Latex #2 was "Chemisat LCH-7505X," which is a highly saturated carboxylated butadiene/acrylonitrile copolymer latex available from the Goodyear Tire & Rubber Co., Akron, Ohio.

- 5) Defoamer #1 was "Patcote 519," which is a defoamer available from Patco Chemicals, Kansas City, Missouri.
- 6) Defoamer #2 was "BYK 024," a defoamer available from BYK Chemie USA, 524 South Cherry Street, Wallingford, Connecticut 06492.
- 7) The surfactant was "Triton CF-10," a surfactant available from Union Carbide Co., 39 Old Ridgebury Road, Danbury, Connecticut 06817.
- 8) The "conductive spheres" were silver coated microspheres available from Spectro Dynamics Systems, Hickory, North Carolina.
- 9) The graphite component was Natural Flake available from Ashbury Graphite Mills, Ashbury, New Jersey.

A preliminary evaluation was made of a coating of the present invention similar to Example 1 as a flex-circuit impedance matching coating. The impedance versus frequency of the coated tape varied between about 25 and 40. All of the data was for both sides coated, one central signal run between two shield runs, but neither coating shorted to the shields. The ideal transmission line will have a broad band of constant impedance (generally at 50 or 75 ohms) versus frequency. Against this criterion, the coating of the present invention was

comparable to other impedance matching coatings. Some of the impedance variation may have been due to the inconsistent thickness of the coating on the test sample. The coating varied from 0.0045" to 0.0145" thick with an average thickness of 0.0063". Improved application methods, such as spray or screen printing, will enable improved thickness control., The coating represents a much higher resistance coating than other coatings previously evaluated. The volume resistivity is approximately 2800 milliohn-cm, compared to 1.2 milliohn-cm of another coating and 0.2 milliohn-cm of yet another coating. Since the impedance reduction is comparable for these coatings of vastly different conductivity, it appears that the impedance depression effect is not highly sensitive to coating resistance, at least in the range of several hundred ohms per inch.

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While certain representative embodiments and details have been shown for the purpose of illustrating the invention, it will be apparent to those skilled in this art that various changes, modifications and variations may be made therein without departing from the scope of the invention. Accordingly, it is intended to embrace all such changes, modifications and variations that fall within the spirit and scope of the appended claims. All patent applications, patents and other publications cited herein are incorporated by reference in their entirety. All parts and percentages are by weight unless otherwise explicitly stated.

#### I CLAIM:

1. A coating composition having electrically conductive and electromagnetic radiation absorptive properties, comprising:

- (1) a water soluble emulsion polymer binder, the binder being a blend of
- (a) a first emulsion containing a polymer prepared from 5 to 100 percent by weight of a conjugated diene monomer or comonomer and 95 to 0 percent by weight of an ethylenically unsaturated comonomer, and
- (b) a second emulsion containing an acrylic polymer;
- (2) an effective amount of electrically conductive particles dispersed in the binder, the particles including a combination of
  - (a) graphite particles, and
  - (b) metal containing particles; and
  - (3) a solvent effective amount of water.
- 2. The coating composition of claim 1, wherein the conjugated diene is but adiene comonomer and the first emulsion includes the ethylenically unsaturated comonomer.
- 3. The coating composition of claim 2, wherein the ethylenically unsaturated comonomer is an unsaturated nitrile, a monovinyl aromatic hydrocarbon or vinylpyridine.

4. The coating composition of claim 3, wherein the ethylenically unsaturated comonomer is acrylonitrile, styrene or vinylpyridine.

- 5. The coating composition of claim 1, wherein the first emulsion is a substantially saturated carboxylated or non-carboxylated butadiene-acrylonitrile latex.
- 6. The coating composition of claim 5, wherein the carboxylated butadiene-acrylonitrile latex contains unreacted salts.
- 7. The coating composition of claim 1, wherein the sole essential components are (1), (2) and (3), and wherein the graphite particles are natural flake graphite.
- 8. The coating composition of claim 1, wherein the metal particles are silver or nickel containing particles.
- 9. The coating composition of claim 8, wherein the silver or nickel containing particles are silver or nickel coated ceramic microspheres.
- 10. The coating composition of claim 9, wherein the microspheres are electromagnetic radiation absorptive microspheres.
- 11. A coated substrate, comprising a substrate and the coating composition of claim 1 coated thereon.
- 12. The coated substrate of claim 11, wherein the substrate is paper, cloth, plastic, rubber, steel or fiberglass.

13. The coated substrate of claim 12, wherein the plastic is a polycarbonate, acrylic or nylon plastic.

- 14. The coated substrate of claim 11, wherein the substrate is a plastic component of an electronic device.
- 15. The coated substrate of claim 11, wherein the substrate is a pipe.
- 16. The coated substrate of claim 11, wherein the substrate is a rubber mat.
- 17. The coated substrate of claim 11, wherein the metal containing particles are electromagnetic radiation absorptive microspheres.
- 18. The coated substrate of claim 17, wherein the substrate is a vehicle.
- 19. The coated substrate of claim 17, wherein the substrate is paper and the substrate is coated by adding the coating composition by beater addition or coating the paper with the coating composition after the paper leaves the paper machine.
- 20. A coating composition having electrically conductive and electromagnetic radiation absorptive properties, comprising:
- (1) a water soluble emulsion polymer binder, the binder being a blend of
- (a) a first emulsion containing a polymer of butadiene and ethylenically unsaturated comonomers, and

(b) a second emulsion containing an acrylic polymer;

- (2) an effective amount of electrically conductive particles dispersed in the binder, the particles including a combination of
  - (a) graphite particles, and
- (b) metal containing particles, the metal containing particles being metal coated ceramic microspheres; and
  - (3) a solvent effective amount of water.
- 21. The coating composition of claim 20, wherein the ethylenically unsaturated comonomer is acrylonitrile, styrene or vinylpyridine.
- 22. The coating composition of claim 20, wherein the first emulsion is a substantially saturated carboxylated or non-carboxylated butadiene-acrylonitrile latex.
- 23. The coating composition of claim 20, wherein the metal particles are silver or nickel containing particles.
- 24. The coating composition of claim 20, wherein the microspheres are electromagnetic radiation absorptive microspheres.
- 25. A coated substrate, comprising a substrate and the coating composition of claim 20 coated thereon.
- 26. The coated substrate of claim 25, wherein the substrate is a plastic component of an electronic device.

27. The coated substrate of claim 25, wherein the metal containing particles are electromagnetic radiation absorptive microspheres.

- 28. The coated substrate of claim 27, wherein the substrate is a vehicle.
- 29. A coating composition having electrically conductive and electromagnetic radiation absorptive properties, comprising:
- (1) a water soluble emulsion polymer binder, the binder being a blend of
- (a) a first emulsion which is a substantially saturated carboxylated or non-carboxylated butadiene-acrylonitrile latex, and
- (b) a second emulsion containing an acrylic polymer;
- (2) an effective amount of electrically conductive particles dispersed in the binder, the particles including a combination of
  - (a) natural flake graphite particles, and
  - (b) silver coated ceramic microspheres; and
  - (3) a solvent effective amount of water.
- 30. A coated substrate, comprising a substrate and the coating composition of claim 29 coated thereon.
- 31. An electrically conductive or electromagnet radiation absorptive coating composition of claim 1, wherein the

first emulsion comprises from about 10 to about 600 parts by weight, the second emulsion comprises from about 10 to about 600 parts by weight, the graphite particles comprise from about 1 to about 280 parts by weight, the metal-containing particles comprises from about 1 to about 280 parts by weight, and the solvent effective amount of water, in addition to that in said binder, comprises from about 50 to about 150 parts by weight.

32. A coating composition of claim 31 wherein the first emulsion comprises from about 300 to about 500 parts by weight, the second emulsion comprises from about 100 to about 300 parts by weight, the graphite particles comprise from about 20 to about 200 parts by weight, the metal-containing particles comprise from about 20 to about 200 parts by weight, and the solvent effective amount of water, in addition to that in said binder, comprises from about 75 to about 125 parts by weight.

### INTERNATIONAL SEARCH REPORT

mai Application No PCT/US 02/07039

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C09D5/24 C09D C09D133/06 C09D109/00 C09D5/32 C09D5/02 According to Internetional Patent Classification (IPC) or to both national classification and IPC B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) CO9D CO8K IPC 7 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical search terms used) EPO-Internal, WPI Data, PAJ C. DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document, with indication, where appropriate, of the relevant passages Relevant to daim No. Category ° X EP 0 591 815 A (ROEHM GMBH) 1-4,11, 12,31,32 13 April 1994 (1994-04-13) page 4, line 36 -page 5, line 44 page 6, line 33 - line 43 1-32 examples 1,5 claims 1-8 EP 0 450 701 A (ARMITAGE & CO JOHN L) 9 October 1991 (1991-10-09) Y 1-32 page 3, line 8 - line 41 page 4, line 3 - line 8 examples 2-6 claims 1-9,18-23 Further documents are listed in the continuation of box C. Patent family members are listed in annex. Special categories of cited documents: "T" later document published after the International filing data or priority date and not in conflict with the application but alled to understand the principle or theory underlying the "A" document defining the general state of the art which is not considered to be of particular relevance invention 'E' earlier document but published on or after the international "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone filma date "L" document which may throw doubts on priority claim(s) or which is clied to establish the publication date of another citation or other special reason (as specified) "Y" document of particular relevance; the datimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "O" document referring to an oral disclosure, use, exhibition or other means document published prior to the international fliing date but later than the priority date claimed \*&\* document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 5 November 2002 18/11/2002 Name and mailing address of the ISA Authorized officer European Patent Office, P.B. 5818 Patentiaan 2 NL - 2280 HV Risawijk Tel. (+31-70) 340-2040, Tx. 31 651 epo ni, Denis, C

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